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(21) International Application Number: PCT/NL97/00677 (22) International Filing Date: 9 December 1997 (09.12.97) (30) Priority Data: 1004738 10 December 1996 (10.12.96) NL (71) Applicant (for all designated States except US): COOPERATIE COSUN U.A. [NL/NL]; Oostelijke Havendijk 15, P.O. Box 1308, NL-4700 Roosendaal (NL). (72) Inventors; and (75) Inventors/Applicants (for US only): KUZEE, Hendrika, Cornelia [NL/NL]; Kanaalstraat 57, NL-4388 BK Oost Souburg (NL). BOLKENBAAS, Mariëtte, Ellen, Boukje [NL/NL]; Groene-Poort 3, NL-4307 AA Oosterland (NL). RAAIJMAKERS, Henricus, Wilhelmus, Carolina [NL/NL]; Jagersingel 41, NL-5241 JW Rosmalen (NL). (74) Agent: DE BRUIJN, Leendert, C.; Nederlandsch Octrooibureau, Scheveningsweg 82, P.O. Box 29720, NL-2502 LS The Hague (NL).		(81) Designated States: AU, CA, JP, NZ, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: FRUCTAN-POLYCARBOXYLIC ACID (57) Abstract Fructan-polycarboxylic acids and salts thereof wherein at least 0.05 of every 3 hydroxymethyl(ene) groups of the fructan has been converted into a carboxyl group and at least 0.1 of every 3 hydroxyl groups has been converted into a carboxymethoxy (or other carboxyalkyl or carboxyacyl) group have an improved action as crystal growth-inhibiting, calcium-binding and/or -dispersing agents. The fructan-polycarboxylic acids can be prepared in that a fructan is oxidised and the oxidation product is then carboxymethylated, or is first carboxymethylated and then oxidised.		

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Fructan-polycarboxylic acid

The invention relates to fructan-polycarboxylic acids.

WO 91/17189 discloses fructan-polycarboxylic acids in the form of polycarboxyinulin, which is also designated as dicarboxyinulin (DCI). In DCI the C3-C4 bond of the oxidised anhydrofructose unit has been broken with the formation of units having the formula: $[\text{HOCH}_2-\text{CH}(\text{COO}^-)-\text{O}-\text{C}(\text{COO}^-)-\text{CH}_2-\text{O}]_n$. According to WO 91/17189, DCI is obtained by oxidation of inulin with a hypohalite. DCI having a degree of substitution (DS: number of carboxyl groups per monosaccharide unit) of the order of 1-2 has a good calcium-binding capacity.

According to WO 94/21690, DCI can be prepared by oxidation of inulin with hydrogen peroxide in the presence of a halide salt and/or a transition metal salt. According to *Starch/Stärke* 41, 348 (1989), DCI can be prepared by treatment with periodate, followed by treatment with chlorite.

WO 95/07303 discloses a method for the oxidation of inulin, wherein predominantly the primary hydroxyl group is oxidised to a carboxyl group with hypohalite in the presence of a di-tert-alkylnitroxyl such as TEMPO (tetramethylpiperidin-1-oxyl).

Carboxymethylinulin having a DS of 0.15-2.5 is disclosed in WO 95/15984 and in the article by Verraest et al. in *JAOCS*, 73 (1996) pp. 55-62. It is prepared by reaction of a concentrated solution of inulin with sodium chloroacetate at elevated temperature. Carboxymethylinulin (CMI) has advantageous properties as an inhibitor of the crystallisation of calcium carbonate.

It has now been found that a fructan-polycarboxylic acid which simultaneously contains carboxyl groups obtained by oxidation of carbon atoms forming part of the anhydrofructose units and carboxyalkyl or carboxyacyl groups attached to the anhydrofructan units has improved properties in respect of calcium-binding capacity, calcium carbonate-dispersing capacity and crystal growth-inhibiting capacity, which improvements are greater than may be expected from a combination of dicarboxyinulin and carboxymethylinulin. These new products are especially useful in those areas where combinations of EDTA or NTA and phosphonates or polyacrylates are conventionally used; EDTA and NTA only act as sequestering agents, whereas phosphonates and acrylates mainly

function as scale inhibitors.

Where reference is made herein to carboxylic acids, this term always refers to the free acid and to the anion thereof including any metal or ammonium salt thereof. The term carboxyalkyl refers to a C₁-C₄ alkyl group substituted by one or more carboxyl groups, such as carboxymethyl, carboxyethyl, dicarboxymethyl, 1,2-dicarboxyethyl etc. The term carboxyacyl refers to a C₁-C₄ acyl group, especially a C₁-C₄ alkanoyl or alkenoyl group substituted by one or more carboxyl groups, such as carboxyacetyl, β -carboxypropionyl, β -carboxyacryloyl, γ -carboxybutyryl, dicarboxyhydroxybutyryl etc. Among the carboxy-alkyl and carboxyacyl groups, preference is given to carboxymethyl, but where carboxymethyl is generally referred to below, this includes any of the other carboxyalkyl and carboxyacyl groups.

The fructan-polycarboxylic acid according to the invention, or salt thereof, has a degree of substitution by carboxyl groups obtained by oxidation of at least 0.05 per original anhydrofructose unit and a degree of substitution by carboxyalkyl or carboxyacyl groups of at least 0.1 per anhydrofructose unit. The carboxyl groups obtained by oxidation can have been obtained by oxidation of the vicinal hydroxymethylene groups in positions 3 and 4 of the anhydrofructose unit and/or by oxidation of the hydroxymethyl group in position 6 (in inulin; position 1 in levan). The carboxyalkyl or carboxyacyl groups can have been obtained by carboxyalkylation or carboxyacylation, respectively, of one of the three hydroxyl groups of the anhydrofructose unit. Thus, in the fructan-polycarboxylic acid, at least 0.05 of every 3 hydroxymethyl(ene) groups of the fructan has been converted (by oxidation) into a carboxyl group and at least 0.1 of every 3 hydroxyl groups has been converted into a carboxyalkoxy or carboxyacyloxy group, preferably a carboxymethoxy group. Preferably, the number of hydroxymethyl(ene) groups which has been converted into a carboxyl group is at least 0.2 and in particular at least 0.3 in every 3, rising to a maximum of 2.9, in particular a maximum of 2 in every 3. Preferably, the number of hydroxyl groups which has been converted into carboxymethoxy groups is at least 0.3, in particular at least 0.5, rising to 2, in particular to 1.6 in every 3. Preferably, the total degree of substitution (DS) by carboxyl groups is 0.8-3.0, in particular 1.0-2.5. It is also preferable that hydroxymethyl(ene) groups converted into carboxyl groups and hydroxyl groups converted into carboxymethoxy groups are in the same molecule.

In this context fructans are understood to be any oligo- and polysaccharide which has a plurality of anhydrofructose units. The fructans can have a polydisperse chain length

distribution and can be straight-chain or branched. Preferably, the fructan contains mainly β -2,1 bonds, as in inulin, but they may also contain β -2,6 bonds as in levan. The fructans comprise both products obtained directly from a vegetable or other source and the products in which the average chain length has been modified (increased or reduced) by fractionation, enzymatic synthesis or hydrolysis. The fructans have an average chain length (= degree of polymerisation, DP) of at least 2, rising to about 1000. Preferably, the average chain length is at least 3, more preferably at least 6, in particular at least 10 monosaccharide units, up to about 60. In particular, the fructan is inulin (β -2,1-fructan) or a modified inulin. Inulin can be obtained from, for example, chicory, dahlias and Jerusalem artichokes, or genetically modified crops such as sugar beet.

Fructans which can serve as the basis for the fructan-polycarboxylic acids of the invention are, in addition to the naturally occurring and industrial base polysaccharides, for example hydrolysis products, that is to say fructan derivatives having shortened chains, and fractionated products having a modified chain length, in particular having an average chain length of at least 10. Prior hydrolysis for obtaining shorter fructans can be carried out for example enzymatically (endo-inulinase), chemically (aqueous acid) or by heterogeneous catalysis (acid ion exchange, see WO 97/23511). Fractionation of fructans such as inulin can be achieved by, for example, low temperature crystallisation (see WO 96/01849), separation by column chromatography (see WO 94/12541) or membrane filtration (see EP-A-440074 and EP-A-627490) or selective precipitation with an alcohol. Other fructans, such as long-chain fructans which, for example, are obtained on crystallisation, fructans from which mono- and disaccharides have been removed and fructans in which the chain length has been lengthened enzymatically, can also be converted to fructan-polycarboxylic acids. Reduced fructans can also be used. Reduced fructans are fructans in which reducing terminal groups (usually fructose groups) have been reduced, for example using sodium borohydride or using hydrogen in the presence of a transition metal catalyst. Other fructans which have been chemically pre-modified, such as crosslinked fructans and hydroxyalkylated fructans can be used as well, to produce the corresponding modified fructan-polycarboxylic acids.

The fructan-polycarboxylic acids according to the invention can be prepared by oxidation of the fructan in a manner known per se, followed by carboxyalkylation or carboxyacylation in a manner known per se, or by the reverse sequence of treatments. The carboxymethylation can, for example, be carried out using sodium monochloro-

acetate in water at pH 10–13, or using another haloacetic acid derivative. Dicarboxymethylation can be carried out in a similar manner e.g. by reaction with a halomalonate ester followed by hydrolysis. Carboxyacetylation can be performed using an anhydride or other reactive derivative of a polycarboxylic acid, such as succinic or maleic anhydride.

5 The oxidation can be carried out in various ways, for example using hypohalite, using periodate/chlorite or using hydrogen peroxide, which in each case mainly leads to dicarboxyl groups (C3–C4 splitting), or using hypochlorite/TEMPO, which leads to monocarboxyl groups (C6 oxidation), as described in the above-mentioned publications. C3–C4 oxidation is preferred.

10 If the fructan is first carboxymethylated, a DS of no more than 1.2 is preferably achieved by this operation, so that sufficient reaction sites remain for the subsequent C3–C4 oxidation. In the case of subsequent C6 oxidation, the carboxymethylation can also be allowed to proceed to a further extent, for example to a DS of 2.0.

Surprisingly, it was found that products obtained by oxidation and subsequent carboxymethylation display even better calcium binding, calcium carbonate dispersing and crystallisation inhibiting performance than products obtained by oxidation of carboxymethylfructan or the combination oxidised fructan and carboxymethylfructan with the same total carboxyl content. It is preferable therefore first to oxidise the fructan, e.g. to

15 a DS of at least 0.2, for example to a DS of 0.5–2.0 (25–100 % oxidation in case of C3–C4 oxidation). The oxidised product can then be carboxymethylated, for example to a DS of 0.2–1.8, especially 0.5–1.6. If appropriate, the solution obtained on oxidation is concentrated so that the efficiency of the carboxymethylation is increased. This leads to products wherein the carboxymethyl groups have a higher presence on the primary hydroxyl groups (C6 in inulin; C1 in levan) than normally found in carboxymethylated

20 fructans. This corresponds to at least 30%, especially at least 40% of the carboxyalkyl or carboxyacyl groups being present on primary carbon atoms. It is frequently advantageous to use as starting material a fructan from which any reducing units have been removed by treatment with a reducing agent such as sodium borohydride or hydrogen in combination with a transition metal catalyst. An advantageous sequence of

25 treatment is then reduction – oxidation – carboxyalkylation – purification.

30

The fructan–polycarboxylic acids according to the invention have an excellent combination of calcium-binding, calcium carbonate-dispersing and crystal growth-inhibiting properties, as is illustrated in the examples. Consequently, these novel

substances are outstandingly suitable as a multifunctional constituent in cleaning agents. In addition, these fructan-polycarboxylic acids can be used as an auxiliary in detergents, membrane cleaning, water treatment agents, textile treatment agents, in papermaking, in adhesives and in the removal of heavy metals from soil, sludge or other types of sediments.

Examples

General

Determination of calcium-binding capacity (CBC):

The potential of standard 10^{-3} and 10^{-5} M Ca^{2+} solutions (with $5 \cdot 10^{-3}$ N NaCl) is determined using a calcium-selective electrode. Polycarboxylic acid is added to 150 ml 10^{-3} M Ca^{2+} (+ $5 \cdot 10^{-3}$ N NaCl) measurement solution in an amount such that the concentration falls to 10^{-5} M. If x is the required number of grams of polycarboxylic acid, then:

$$\text{CBC} = \{1000 \cdot (10^{-3} - 10^{-5})\} / (1000 \cdot x / 150) \text{ in mmol Ca per g polycarboxylic acid.}$$

15 Determination of calcium carbonate-dispersing capacity (CCDC):

An amount of ≈ 1 g polycarboxylic acid is weighed out accurately and made up to 100.0 g with demineralised water. 10.0 ml 10 % m/v Na_2CO_3 is added thereto and a spectrophotometric immersion cell is placed in the solution. When the transmission of the solution at 700 nm has a constant value, calcium acetate (0.25 M) is added to the stirred solution (300 rpm) in steps of 0.25 or 0.50 ml. The turning point (the point at which the first turbidity appears) is determined from the titration curve. If x ml Ca acetate has been consumed at the turning point, then:

$$\text{CCDC} = (x \cdot 0.25 \cdot 100.08) / (\text{weighed amount of polycarboxylic acid in g})$$

Determination of crystal growth-inhibiting capacity (CGIC) on calcium carbonate:

25 100 ml 0.02 M K_2CO_3 , 100 ml 0.02 M CaCl_2 and 2.0 ml 1000 ppm polycarboxylic acid are added together. The polycarboxylic acid concentration is 10 ppm. The solution is stirred for at least 60 minutes using a magnetic stirrer (800 rpm) at a constant

temperature of 20 °C. The particle size in the solution is determined using a Malvern particle size meter (twice for each solution; two solutions, therefore four measurement values). The average particle size D_i is compared with the average particle size D_0 of a solution without polycarboxylic acid. $CGIC = 100 - 100 \cdot D_i / D_0$.

5 Determination of carboxyl content:

The carboxyl content is determined on the basis of the sodium content of the purified end product.

Example 1

Preparation of carboxymethylated DCI:

10 An amount of 210.0 g inulin (standard, chicory, av. DP 10, composition see Table 3, solids content 95 % by weight, 1.2 mol) was dissolved in 667 ml water containing 0.02 M NaBr. 800.8 g sodium hypochlorite (1.85 mmol NaOCl/g: 1.48 mol = 0.41 eq.) was added to this solution at room temperature in the course of two hours. After a reaction time of 24 hours at < 25 °C and pH 10.5 (pH-stat, 4.0 N NaOH) the alkali
15 consumption was 1040 mmol and no further hypochlorite was detectable. The solution was purified with the aid of the P1 electrodialysis Aqualizer from E.I.V.S. Corning (30V, 20–60 min, electrolyte and salt compartment 1 % NaCl). The purified solution was evaporated to dryness and post-dried in a vacuum oven at 70 °C. Yield 240.3 g; $DS_{COOH} = 0.66$ (degree of oxidation: 33 %; efficiency with respect to hypochlorite:
20 81 %).

Sodium monochloroacetate (NaMCA) (16.3 g, 14 mmol) and sodium hydroxide (6.1 g = 150 mmol) were added as solids to a solution of 40 g (215 mmol) of the DCI thus obtained in 133 ml water (= 30 % m/v) (solids content of the reaction mixture: 39 % by weight). After 4 hours at 60 °C the pH was lowered to 10 using HCl. The degree of
25 substitution by carboxymethyl was determined on the crude product from the difference between the amount of MCA added and the amount of MCA, glycolic acid and oxydiacetic acid (diglycolic acid) found in the reaction product. Result: 66.8 mmol carboxymethyl products: $DS_{CH_2COOH} = 0.32$ $DS_{total} = 0.98$.

The carboxymethylation was repeated except that 35.8 g (= 0.31 mol) and 58.4 g
30 (= 0.50 mol) NaMCA (solids content of mixture 53 % by weight and 67 % by weight

respectively) were used. The DS_{CH_2COOH} obtained is 0.79 and 1.14 respectively.

The carboxymethylated DCI was purified in the same way as DCI (concentration in water: 15 % m/v). Yield 270.3 g : $DS_{COOH} = 0.98$. The other carboxymethylations gave yields of 319.5 and 353.1 g respectively. The physical data are given in Tables 1 and 2 (nos 1, 2 and 3).

Table 1: Properties of oxidised and/or carboxymethylated standard inulin

	DS			% by weight	CBC ¹ mmol Ca/g	CCDC ² mg CaCO ₃ /g	CGIC ³
No.	DCI-COOH	CMI-COOH	COOH total	COOH	(mmol Ca /g COOH)	(mg CaCO ₃ /g COOH)	100-100D _i /D ₀
	Carboxymethylated DCI						
1	0.66	0.32	0.98	19.3	1.1 (5.7)	93 (481)	33
2	0.66	0.79	1.45	23.5	1.4 (6.0)	118 (501)	70
3	0.66	1.14	1.80	26.4	1.5 (5.7)	125 (473)	66
	Oxidised CMI						
11	0.64	0.30	0.94	16.6	0.6 (3.6)	67 (403)	17
12	0.64	0.83	1.47	23.0	0.9 (3.9)	96 (418)	29
13	0.64	1.14	1.78	25.8	1.3 (5.7)	91 (352)	44
	DCI + CMI mixture						
21	0.62	0.38	1.00	21.8	0.6 (2.8)	60 (275)	23
22	0.48	0.95	1.43	28.1	1.0 (3.6)	69 (245)	60
23	0.51	1.13	1.64	27.4	1.1 (4.0)	81 (296)	60
	DCI						
31	0.66	-	0.66	21.0	0.8 (3.8)	88 (418)	17
32	1.14	-	1.14	25.1	1.1 (4.4)	114 (455)	0
33	1.72	-	1.72	34.1	1.5 (4.4)	130 (382)	23
	CMI						
41	-	1.14	1.14	20.7	0.6 (2.0)	25 (121)	50
42	-	1.53	1.53	25.6	0.8 (3.1)	44 (172)	66
43	-	2.00	2.00	27.0	1.3 (4.8)	56 (208)	66

¹ Calcium-Binding Capacity in mmol Ca per g product (and per g carboxyl)

² Calcium Carbonate-Dispersing Capacity in mg CaCO₃ per g product (and per g carboxyl)

³ Crystal Growth-Inhibiting Capacity: degree of particle size reduction: CGIC = 0: no reduction, CGIC = 100: complete inhibition

Table 2: Properties of carboxymethylated oxidised inulin

No.	DS carboxymethylated DCI			% by weight	CBC (1) mmol Ca/g	CCDC (2) mg CaCO ₃ /g	CGIC (3)
	DCI- COOH	CMI- COOH	COOH total	COOH	(mmol Ca /g COOH)	(mg CaCO ₃ /g COOH)	100- 100D _f /D ₀
	Standard inulin (av. DP = 10)						
1	0.66	0.32	0.98	19.3	1.1 (5.7)	93 (481)	33
2	0.66	0.79	1.45	23.5	1.4 (6.0)	118 (501)	70
3	0.66	1.14	1.80	26.4	1.5 (5.7)	125 (473)	66
	Precipitate low-temp. cryst. (av. DP = 30)						
101	0.60	0.48	1.08	21.2	1.1 (5.2)	94 (110)	0
102	0.60	0.97	1.57	25.6	1.3 (5.1)	106 (414)	29
103	0.60	1.20	1.80	26.2	1.5 (5.7)	119 (454)	44
	Filtrate l.t. cryst. + nanofilt. (av. DP = 10)						
201	0.62	0.43	1.05	20.9	0.8 (3.8)	81 (388)	41
202	0.62	1.04	1.66	26.4	1.2 (4.5)	88 (333)	60
203	0.62	1.28	1.90	28.5	1.3 (4.6)	99 (347)	60

Table 3: Composition of various types of inulin

Composition (%)	Standard inulin	Precipitate from low-temperature crystallisation	Filtrate from low-temperature crystallisation
Glucose	0.5	0.05	2.2
Fructose	2.3	0.1	8.0
Disaccharides	4.3	0.05	8.8
Trisaccharides	2.8	0.05	5.3
Tetrasaccharides	3.5	0.05	6.5
Pentasaccharides	6.1	0.2	11.2
DP > 5	76.1	99.5	58
Average DP	10	30	7

Example 2*Scale inhibition using oxidised and carboxymethylated inulin*

A volume of 35 ml of a stock solution of 330 mg/l CaCl₂·2H₂O, pH adjusted 10.0 with NaOH, was placed in a 100 ml conical flask. An inhibition solution containing 375 mg

of dry sodium inulin-polycarboxylate (pH 10.0) per l was added in an amount of 1 or 2 ml (corresponding to 5 or 10 ppm of active material). Then 35 ml of a stock solution containing 216 mg/l of Na₂CO₃ (pH 10.0) was added and the flask was stoppered and shaken in a thermostated bath at 66°C for 20 hours. The solution was then cooled to room temperature and filtrated. The filtrate was assayed on calcium content. The inhibition percentage (% inh.) was calculated using the following formula:

$$\% \text{ inh.} = \frac{\text{Ca content with inhibitor} - \text{Ca content without inhibitor}}{\text{Ca content at start} - \text{Ca content without inhibitor}} \times 100\%$$

The following inulin-polycarboxylic acids were used: dicarboxyinulin (DCI), carboxy-methyl-inulin (CMI), an equimolar mixture of DCI and CMI (DCI/CMI), carboxy-methylated dicarboxyinulin (CMDCI) and C3-C4 oxidised carboxymethyl-inulin (DCCMI), each with a total average carboxyl DS of about 1.6. The results are given in table 4.

Table 4: Scale inhibition of carboxy-inulin

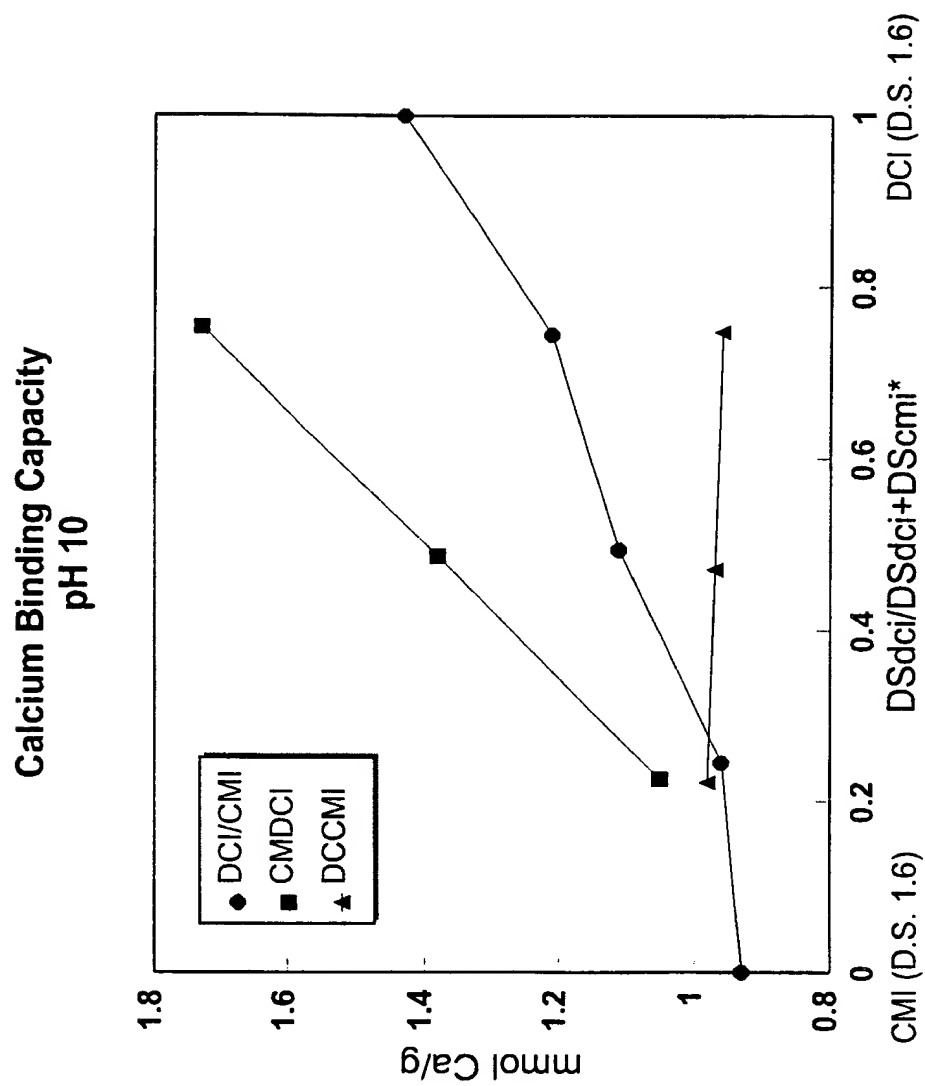
carboxyinulin	DS-DCI	DS-CMI	DS total	% inhibition	
				5 ppm	10 ppm
DCI	1.56	–	1.56	3	5
CMI	–	1.60	1.60	89	100
DCI/CMI	0.78	0.80	1.58	65	85
CMDCI	0.76	0.80	1.56	85	97
DCCMI	0.74	0.83	1.57	49	73

Figures 1, 2 and 3 depict the calcium binding capacity, the calcium carbonate dispersing capacity and the calcium carbonate crystal growth inhibition capacity, respectively, of CMI, DCI, 3:1, 1:1 and 1:3 mixtures of CMI and DCI, CMDCI and DCCMI, the latter two with carboxymethyl:oxidised-carboxy ratios of 3:1, 1:1 and 1:3, and all five with total carboxyl DS of 1.6. The figures show that CMDCI performs better, sometimes dramatically better, in all three properties than the foreseeable values which would be situated on a straight line between the values for CMI and DCI. For DCCMI and the DCI/CMI mixture, it depends on the specific property and on the carboxyl ratio, whether they perform better than expected.

Claims

1. A fructan-polycarboxylic acid or salt thereof, wherein at least 0.05 of every 3 hydroxymethyl(ene) groups of the fructan has been converted to a carboxyl group and at least 0.1 of every 3 hydroxyl groups has been converted to a carboxy-alkoxy or carboxy-acyloxy group.
5
2. A fructan-polycarboxylic acid or salt thereof, wherein 0.2–2.0 of every 3 hydroxymethyl(ene) groups of the fructan have been converted to a carboxyl group and 0.3–2.0 of every 3 hydroxyl groups have been converted to a carboxymethoxy group.
3. A fructan-polycarboxylic acid according to Claim 1 or 2, wherein hydroxymethyl(ene) groups converted to carboxyl groups and hydroxyl groups converted to carboxy-alkoxy or carboxy-acyloxy groups are present in the same molecule.
10
4. A fructan-polycarboxylic acid according to any one of Claims 1–3, wherein the total degree of substitution (DS) by carboxyl groups is 0.15–3.0.
5. A fructan-polycarboxylic acid according to any one of Claims 1–4, wherein at least 30% of the carboxy-alkoxy or carboxy-acyloxy groups are present on primary carbon atoms of the fructan.
15
6. A process for preparing a fructan-polycarboxylic acid, wherein a fructan or a derivative thereof is subjected to carboxyalkylation or carboxyacylation and oxidation.
7. A process according to claim 6, wherein the fructan is first oxidised and the oxidation product is carboxymethylated.
20
8. A process according to Claim 6 or 7, wherein the carboxyalkylation is carried out to a degree of substitution of 0.1–2.0.
9. A process according to any one of Claims 6–8, wherein the oxidation is carried out using a hypohalite.
10. A process according to Claim 9, wherein the oxidation is carried out in the presence of a di-tert-alkylnitroxyl.
25

11. A process according to any one of Claims 6-10, wherein the fructan is reduced prior to the oxidation and carboxyalkylation or carboxyacylation.
12. A crystal growth-inhibiting, calcium-binding and/or -dispersing agent which contains a fructan-polycarboxylic acid according to any one of Claims 1-5.
- 5 13. Use of a fructan-polycarboxylic acid according to one of Claims 1-5 in detergents, cleaning agents, water treatment agents, textile treatment agents, in paper-making, in adhesives and in the removal of heavy metals.



*: at constant DS of 1.6

Figure 1

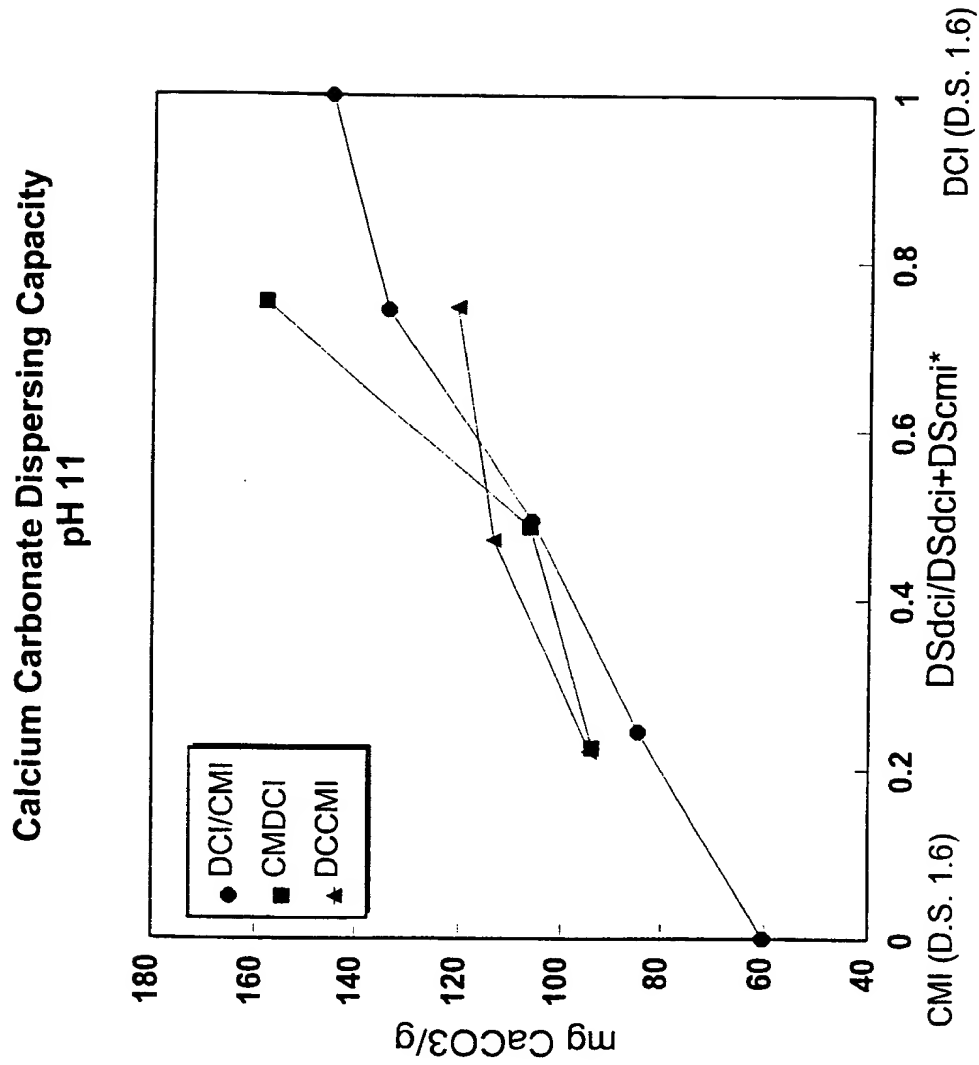
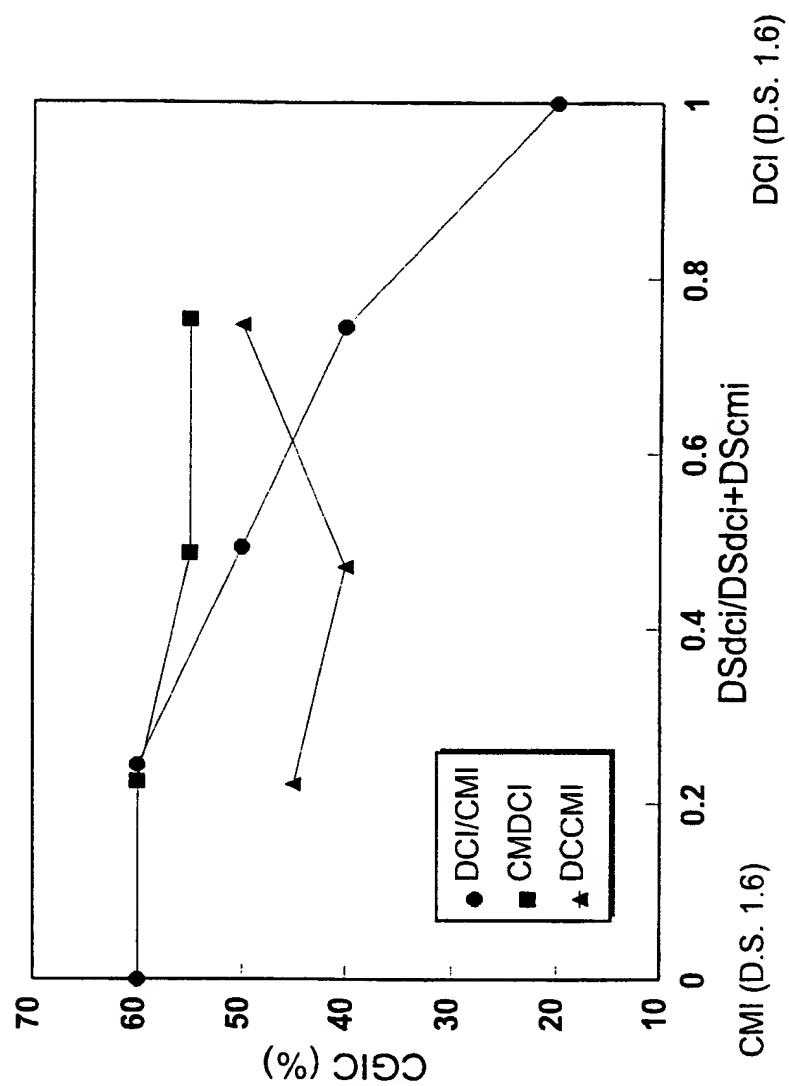


Figure 2

Crystal Growth Inhibition of Calcium Carbonate



*: at constant DS of 1.6

Figure 3

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/NL 97/00677

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08B37/18

According to International Patent Classification (IPC) or to both national classification and IPC

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Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	D.L. VERRAEST ET AL.: "Oxidation and carboxymethylation of sucrose and inulin" ZUCKER INDUSTRIE, vol. 120, no. 9, September 1995, DE, pages 799-803, XP002037421 see the whole document -----	1-13



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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Date of the actual completion of the international search

26 March 1998

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03/04/1998

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